PATENT ABSTRACTS OF JAPAN

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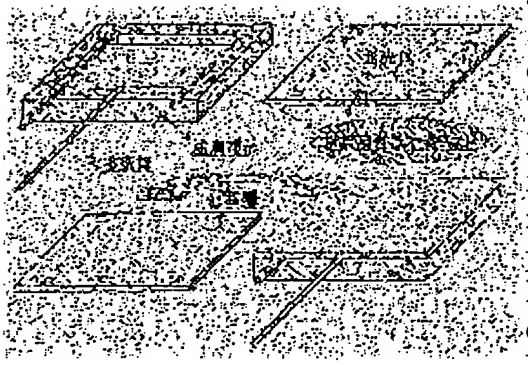
(54) LEAD-FREE LOW MELTING POINT GLASS FOR SEALING

(57)Abstract:
PROBLEM TO BE SOLVED: To provide lead-free glass for sealing electronic components such as a fluorescent display tube, a fluorescent tube and a semiconductor package in particular.
SOLUTION: The lead-free glass for sealing is equal to lead-containing low melting point glass. The lead-free glass for sealing is a composition of lead-free metal oxide consisting of a network former oxide, an intermediate oxide and a network modifier oxide, and is obtained by preparing the oxides in prescribed weight%. The lead-free glass composed of a lead-free composition in which the network former oxide is V2O5, the intermediate oxide is ZnO, and the network modifier oxide is BaO or TeO2 is excellent in thermal properties and sealing performance.



[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs]
This invention relates to the closure of electronic parts especially a fluorescent indicator tube, fluorescence tubing, and the low-melt point point nonlead glass for sealing

processing of a semiconductor package.
[0002]
[Description of the Prior Art]
Conventionally, sealing processings are a series of activities which are used in the field of the electronics industry, stop opening of a metal, glass, or a ceramic container, and prevent invasion of gas or moisture. In order that sealing may guarantee stable actuation of the electron tube or electronic parts, it is an indispensable activity, and the lead glass of the shape of powder containing current and lead oxide (PbO) is used. The glass of 2OPbO-B3 system with which the principal component of lead glass harnessed the low melting point nature of PbO and high solubility was a core (for example, patent reference 1 and 2).
[0003]
However, the venenosity which lead has in recent years is posing a problem. It is said that it will commit the increment in a denaturation corpuscle, reduction of hemoglobin, and a brain center, and will produce Alzheimer's disease in a hematogenous enzyme failure and an erythrocyte if this lead is taken in by the body. Lead exists also in the usual environment widely, exists also in the body, is always taken in and excreted (80mg of body Nakahira **, 70kg), and its intake is abundant and it is poisoned when accumulated in the inside of the body. When the electronic parts which furthermore used lead glass as sealing material are discarded, lead permeates underground by acid rain and the harmful nature is regarded as questionable as it is what leads also to soil pollution and groundwater contamination. For this reason, atmospheric control has also been carried out with the regulation from the Occupational Safety and Health side which prevents an occupational disease.
[0004]
The development of the glass for sealing of an owner lead system and the glass for sealing of the unleaded system for which it can be substituted currently used for old various electronic parts from such a background is demanded.
[0005]
The research report is made about TiO2 system, 2OP5 system, etc. as unleaded system low melting glass until now, and it is shown clearly that what is low-melting can be prepared. However, low-fever expansion, an adhesive property, closure nature, and the glass for sealing of the unleaded system which was further excellent in chemical durability have not yet escaped from the field of a fundamental research, so that it can substitute completely with owner lead system glass.
[0006]
[Patent reference 1]
JP,2000-113820,A
[Patent reference 2]
JP,8-180837,A
[0007]
[Problem(s) to be Solved by the Invention]
This invention not only by the mere element permutation but by ingredient retrieval based on the physicochemical quality of the element which constitutes glass structure and it By the difference in the organization potency force of the glass by single bond reinforcement with oxygen, a metallic oxide A mesh formation oxide (Network former :

NWF), It aims at obtaining the glass for sealing which matched or was excellent in lead system low melting glass paying attention to being classified with an intermediate oxide (Intermediate) and a mesh modifier oxide (Network modifier : NWM).
[0008]
[Means for Solving the Problem]
It is this invention in order to attain the above-mentioned purpose.
Unleaded low melting glass for sealing processing which consists [1] of a presentation of weight % of the metallic oxide of four components ofV2ndO5, and ZnO, BaO and TeO2,
Unleaded low melting glass for sealing processing given [above-mentioned] in the 1st invention which made 1 weight the unleaded low melting glass which consists [2] of a presentation of weight % of the metallic oxide ofV2ndO5 and three components of ZnO and BaO, carried out weight % addition of TeO2 to 1 weight of the three components, and was prepared,
the 3rd -- 16 to 80% of the weight of V2O5 and 0 to 40% of the weight of ZnO, 4 to 50% of the weight of BaO, and the unleaded low melting glass for sealing processing given [above-mentioned] in the 1st invention it is unstated from the metallic oxide of four components of TeO2 zero to 60% of the weight,
The above 1st which made 1 weight the unleaded low melting glass set to the 4th from 40 to 80% of the weight of V2O5 and 0 to 40% of the weight of ZnO, and 10 to 50% of the weight of BaO, and added and prepared 1 to 60% of the weight of TeO2 to 1 weight of the three components, or unleaded low melting glass for sealing processing given in the 2nd invention,
Unleaded low melting glass for sealing processing which grinds and classifies [5th] the unleaded low melting glass of a publication up to 0.05 to 100 micrometer in either the above 1st - the 4th invention, makes this 1 weight, adds a low expansion ceramic filler up to zero to 1.5 weight, and becomes as powder,
Unleaded low melting glass for sealing processing which mixes a binder to unleaded low melting glass given in either the 6th above 1st - the 5th invention, and becomes as a paste for sealing processing,
The vacuum package which consists of glass, ceramics, and a metal is sealed [7th] using the paste for sealing processing given [above-mentioned] in the 6th invention, and it is 10-6. The high vacuum more than Torr is realized and it is unleaded low melting glass for sealing processing which can close discharge gas, such as an argon, Xe-Ne, and Ne-Xe-Ar,
Unleaded sealing glass for sealing processing given [above-mentioned] in the 6th invention which can sealing process the vacuum package which performs this baking near crystallization initiation temperature (it borders on crystallization initiation temperature - 20 - +50 degrees), and consists of glass, ceramics, and a metal after performing temporary baking to the 8th near softening temperature (it borders on softening temperature temperature - 10 - +40 degrees),
Be alike is constituted.
[0009]
In addition, on the occasion of preparation of the low melting glass of a unleaded system, ZnO, BaO, and TeO2 were chosen as V2O5 and a mesh modifier oxide as a mesh formation oxide, the unleaded system low melting glass of this 4 component system was

prepared, and structural analysis by the glass transition point, softening temperature, the coefficient of thermal expansion, and powder X-ray diffractometry (XRD) estimated the physicochemical property of the low melting glass of a unleaded system.

[0010]

[Embodiment of the Invention]

the oxide which can form the three-dimension mesh which an oxide with a mesh formation oxide (NWF), i.e., glass organization potency, makes, i.e., the oxide which can form the frame of glass (amorphous substance: amorphous), -- B-2s O3 and V2 -- they are O5, SiO2, and P2O5 grade.

[0011]

an intermediate oxide, i.e., the oxide which replaces some mesh formation oxides (NWF), and joins mesh formation, and can also play a role of a mesh modifier oxide although glass cannot be formed if independent, -- ZnO, PbO, and aluminum2 -- they are O3, TeO2, and Bi2O3 grade.

[0012]

Although glass formation cannot be performed in a mesh modifier oxide (NWM), i.e., independent, the oxides which can enter into the mesh which a mesh formation oxide (NWF) makes as one component of glass, and can affect a property are BaO, ZnO, PbO, TeO2, and Bi2O3 grade.

[0013]

V2O5, and ZnO, BaO and TeO2 are chosen from the above-mentioned physicochemical standpoint as a raw material metallic oxide, and the nonlead glass for sealing processing is prepared.

[0014]

After preparing the nonlead glass for sealing processing which consists of a metallic oxide of three components of V2O5-ZnO-BaO, low-melt point point-ization is realizable by adding the metallic oxide (for example, Bi 2O3 and TeO2) which can realize low-melt point point-ization as the 4th component. In addition, when it prepares as four components of V2O5-BaO-ZnO-TeO2, low-melt point point-ization can be realized.

[0015]

In order to make the coefficient of thermal expansion of the above-mentioned unleaded system low melting glass the same as the coefficient of thermal expansion of a sealing-ed object, and in order to raise the reinforcement of a sealing object, optimal amount addition mixing of the refractories filler is carried out at the above-mentioned low melting glass.

[0016]

As refractories filler powder, there are a KOJIE light, phosphoric-acid zirconyl, beta-you chestnut PUTATO, beta-spodumene, zircon, an alumina, a mullite, a silica, beta-quartz solid solution, silicic-acid zinc, aluminum titanate, etc.

[0017]

The mixed approach of low-melting-glass powder and refractories filler powder is very good in what kind of approach. In case a grinder grinds the low-melt point point glass block prepared and built, refractories filler powder may be added, and grinding and mixing may be performed. Moreover, to the particle size of arbitration, a refractories filler may be added after grinding low melting glass, it may mix, and you may use.

[0018]

The case where a low expansion ceramic filler is not added is 0. Since this does not need to add a low expansion ceramic filler when the coefficient of thermal expansion of a sealing-ed object is equal to the coefficient of thermal expansion of unleaded low melting glass itself, a ceramic filler may be 0.

[0019]

A glass paste mixes the vehicle and the granulated glass for sealing which used celluloses as the binder, and is viscosity 100-2000 It adjusts to dPa-s. The vehicle which used acrylic resin as the binder as a binder may be used. Here, celluloses show a nitrocellulose and ethyl cellulose. The vehicle which uses celluloses as a binder consists of ethyl cellulose, pineapple oil, butyl diethylene glycol acetate, and aromatic hydrocarbon. The vehicle which uses acrylic resin as a binder consists of a solvent of acrylic resin, a ketone, ester, or low-boiling point aromatic series.

[0020]

The adjusted glass paste is applied to fluorescence tubing (drawing 1) which consists of two sheet glass of soda lime glass at homogeneity. Temporary baking is performed for two sheet glass which applies a glass paste with the constant temperature near softening temperature (Tf) in an electric furnace for 15 to 180 minutes. Then, an exhaust pipe is built into two sheet glass picked out from the electric furnace, and a two metal-electrodes list, and it fixes with a clip, and puts into an electric furnace again, and this baking is performed for 15-180 minutes with the constant temperature near crystallization initiation temperature (Tx). Up to 0.05 to 100 micrometer, the unleaded low melting glass used here is ground, and classifies, and what made this 1 weight and was added up to 0 -1.5 weight as a low expansion ceramic filler is used as a glass paste. A fluorescent substance uses what is applied to homogeneity for the fluorescence tube plate glass of two more sheets.

[0021]

In the case of temporary baking, the temperature up process of a multistage story is especially needed near a glass transition point and near softening temperature unleaded low melting glass. They are 0.1-10 degree C/min to near glass transition temperature from 0.1-30 degree C/min, and near glass transition temperature to [from a room temperature] near softening temperature temperature. That is, this actuation is needed in order to prevent forming pores, such as a pinhole, in a sealing glass paste by flying gently the vehicle which dissolved and prepared the binder to the organic solvent according to a multistage story temperature up. About this baking, a temperature up is carried out from a room temperature to near crystallization initiation temperature by 0.1-50 degree C/min, and sealing is performed by holding uniformly near crystallization initiation temperature.

[0022]

Exhaust air processing is performed heating at 50 to 400 degree C using a vacuum pump from the exhaust pipe of sealed fluorescence tubing (drawing 1). It controls to become the high vacuum of 10 to 6 or more Torrs about a degree of vacuum.

[0023]

After setting the degree of vacuum of sealed fluorescence tubing (drawing 1) to 10 to 6 or more Torrs, the mixed discharge gas of Xe-Ar (xenon-argon) is enclosed as discharge gas. Argon gas single gas is sufficient as discharge gas. Moreover, mixed discharge gas may be Ne(neon)-Xe-Ar.

[0024]

It is input power 0.1-1 by pulse drive enclose discharge gas, leave closed fluorescence tubing in the state of un-switching on the light under atmospheric air, and according discharge between the metal electrode (drawing 1) to an inverter the whole predetermined time. The luminescence lighting check of fluorescence tubing is performed in W.

[0025]

[Example]

This invention is not restricted by those examples, although an example is shown below in order to clarify the description of this invention further.

[0026]

Example 1 Preparation of unleaded low melting glass (1) (V2O5-ZnO-BaO-TeO24 component system glass preparation)

What mixed enough the raw material metallic oxide (V2O5, ZnO, BaO, TeO2) of four components by the predetermined presentation shown in Table 1 was put into the platinum crucible, and it calcinated for 60 minutes at about 1000 degrees C within the electric furnace. Then, melt was slushed into the alumina board and the glass rod was produced. The stamp mill ground the glass rod after cooling under atmospheric air, and the particle size was classified in 100 micrometers or less. When prepared by 4 component system, recovery of glass melt was 85%. The appearance of the prepared glass melt is a black (green) color, and was excellent in the fluidity.

[0027]

[Table 1]

		V-Te0	V-Te10	V-Te20	V-Te30
4成分の仕込組成 (wt%)	V_2O_5	60	54	48	42
	ZnO	10	9	8	7
	BaO	30	27	24	21
	TeO_2	0	10	20	30
ガラス転移点 Tg(℃)		280	290	291	285
軟化点 Tf(℃)		310	310	311	310
結晶化開始温度 Tx(℃)		381	392	415	427
熱的安定性⊿T(℃)		101	102	124	142
熱膨張係数($\times 10^{-7}$/℃)		108.0	154.9	133.1	172.8
流動性		○	○	○	○
外観		黒(緑)色	黒(緑)色	黒(緑)色	黒(緑)色
構造		非晶質	非晶質	非晶質	非晶質

[0028]

Example 2 Preparation of unleaded low melting glass (2) (it is a 4th component TeO2 addition system after V2O5-ZnO-BaO3 component system glass preparation)

The raw material metallic oxide (V2O5, ZnO, BaO) which consists of a predetermined

presentation shown in Table 2 was mixed enough, and it put into the platinum crucible, and calcinated for 60 minutes at about 1000 degrees C within the electric furnace. Then, melt was slushed into the alumina board and the glass rod was produced. The stamp mill ground the glass rod after cooling in atmospheric air. This grinding object was enough mixed with TeO2, and it put into the platinum crucible, and slushed into the alumina board within the electric furnace, and the glass rod was produced. The stamp mill ground the glass rod after cooling in atmospheric air, and the particle size was classified in 100 micrometers or less. The recovery of the glass which added and prepared TeO2 as the 4th component was 70% after preparing the glass of 3 component system (V2O5, ZnO, BaO). The appearance of the prepared glass melt is a black (green) color, and was excellent in the fluidity.

[0029]

[Table 2]

		V'-Te10	V'-Te20	V'-Te30
3成分の仕込組成 (wt%)	V_2O_5	54	48	42
	ZnO	9	8	7
	BaO	27	24	21
第4成分の添加量(wt%)	TeO_2	10	20	30
ガラス転移点 Tg(℃)		298	280	293
軟化点 Tf(℃)		312	310	320
結晶化開始温度 Tx(℃)		400	409	430
熱的安定性⊿T(℃)		102	129	139
熱膨張係数($\times 10^{-7}$/℃)		121.8	119.9	135.1
流動性		○	○	○
外観		黒(緑)色	黒(緑)色	黒(緑)色
構造		非晶質	非晶質	非晶質

[0030]

Example 3 Thermal-expansion characterization after ceramic filler mixing to unleaded low melting glass

It is necessary to fit a coefficient of thermal expansion with unleaded low melting glass with a sealing-ed object, to control the stress (stress) of the sealing section, and to consider as a firm sealing object. For example, the case where soda lime glass was selected as a sealing-ed object was made applicable to evaluation. 40 % of the weight of zircon was mixed as a ceramic filler to 60% of the weight of V'-Te30 of Table 2 as the example. As a result of measuring the coefficient of thermal expansion in that case, it was abbreviation 72.5x10-7/degree C. This value was a suitable value when joining to soda lime glass etc.

[0031]

Example 4 Paste preparation
It mixed with the nonlead glass for sealing processing containing a ceramic filler which prepared the vehicle which used ethyl cellulose as the binder by [0030]. viscosity -- 1050 dPa-s it was .
[0032]
Example 5 Sealing processing
The paste prepared by [0031] was applied to the fluorescence tubing package as shown in drawing 2 . Sealing was performed according to the temperature profile who shows drawing 3 .
[0033]
Example 6 Lighting experiment
Exhaust air processing of the degree of vacuum was carried out at 10 to 6 or more Torrs, heating at 350 degrees C with a vacuum pump using the fluorescence tubing package sealed by [0031]. The afterdischarge gas Xe-Ar was closed so that it might be set to discharge-gas-pressure 40Torr. The inverter performed the lighting check under input power abbreviation 0.6W. The result is shown in drawing 4 and Table 3.
[0034]
[Table 3]

真空度 (Torr)	放電ガス 組成	放電ガス圧 (Torr)	封止後点灯確認			
			0h(直後)	72h	168h	1344h
1.0×10^{-6} 以下	Xe-Ar	40	点灯	点灯	点灯	点灯

[0035]
Example 1 of a trial Measurement of a glass transition point and softening temperature
The glass transition point (Tg) of the prepared low melting glass of a unleaded system, softening temperature (Tf), and crystallization initiation temperature (Tx) were measured using the differential thermal analyzer (drawing 1). All samples are the programming rate of 10 degrees C / min, and performed temperature up measurement to 25-600 degrees C. Alpha-aluminum 2O3 was used for the correlation sample. It is deltaT about the index of the chemical and thermal stability of glass (degree C). = Tx- It computed as Tg. The result is shown in Tables 1 and 2.
[0036]
Example 2 of a trial Measurement of a coefficient of thermal expansion
The coefficient of thermal expansion of the prepared unleaded system low melting glass was measured using the apparatus for thermomechanical analysis. That by which the prepared granulated glass was fused again, it fabricated to the 5x5x20mm (vertical x horizontal x height) square pole, and the raised bottom side was fabricated in parallel was used as a test portion. The temperature up was carried out by 5 degrees C / min to 25-200 degrees C, and it asked for the average coefficient of thermal expansion. Alpha-aluminum 2O3 was used for the correlation sample. The result is shown in Tables 1 and 2.
[0037]
Example 3 of a trial Structural analysis by powder X-ray diffractometry (XRD)

Structural analysis of the prepared unleaded system low melting glass was performed using the powder X-ray plant. The scan speed was performed by 2 degrees C / min. The result is shown in Tables 1 and 2.

[0038]

[Effect of the Invention]

Since this invention was constituted as mentioned above, it can obtain the unleaded system low melting glass for sealing processing which matched and was excellent in lead system low melting glass.

[Brief Description of the Drawings]

[Drawing 1] It is sealing process drawing of flat-surface fluorescence tubing.

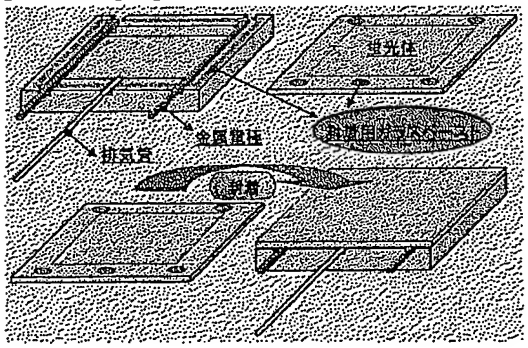
[Drawing 2] They are a glass transition point, softening temperature, and a crystallization initiation temperature curve.

[Drawing 3] A (b) (b) Fig. is a temperature profile who seals flat-surface fluorescence tubing.

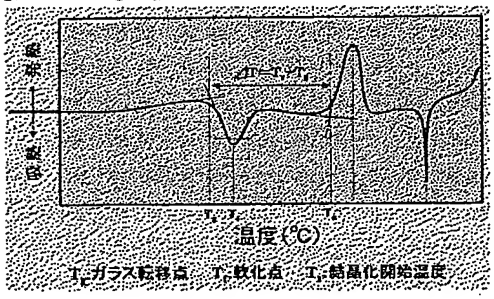
[Drawing 4] A (b) (b) Fig. is in the lighting condition of flat-surface fluorescence tubing.

DRAWINGS

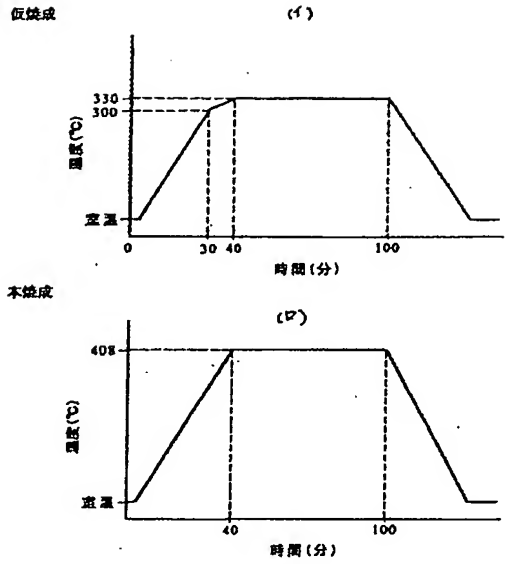
[Drawing 1]



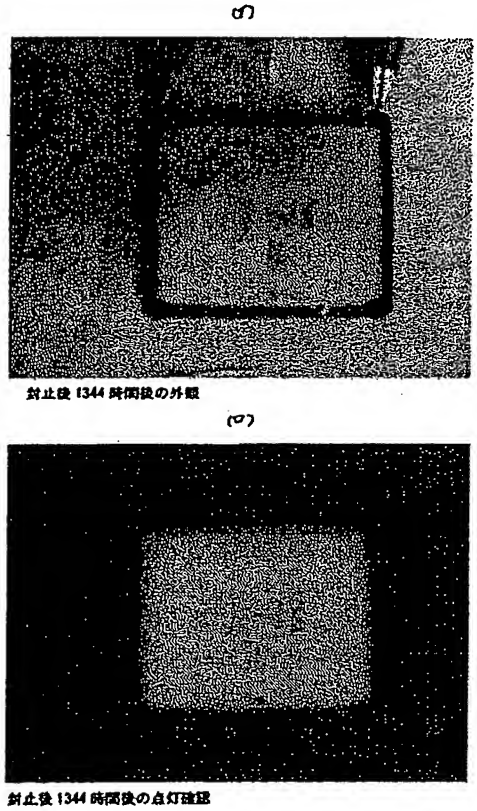
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Claim 1]
Unleaded low melting glass for sealing processing which consists of a presentation of

weight % of the metallic oxide of four components of V2O5, and ZnO, BaO and TeO2.
[Claim 2]
Unleaded low melting glass for sealing processing according to claim 1 which made 1 weight the unleaded low melting glass which consists of a presentation of weight % of the metallic oxide of V2O5 and three components of ZnO and BaO, carried out weight % addition of TeO2 to 1 weight of the three components, and was prepared.
[Claim 3]
16 to 80% of the weight of V2O5 and 0 to 40% of the weight of ZnO, 4 to 50% of the weight of BaO, unleaded low melting glass for sealing processing according to claim 1 that consists of a metallic oxide of four components of TeO2 zero to 60% of the weight.
[Claim 4]
Unleaded low melting glass for sealing processing according to claim 1 or 2 which made 1 weight the unleaded low melting glass which consists of 40 to 80% of the weight of V2O5 and 0 to 40% of the weight of ZnO, and 10 to 50% of the weight of BaO, and added and prepared 1 to 60% of the weight of TeO2 to 1 weight of the three components.
[Claim 5]
Unleaded low melting glass for sealing processing which grinds and classifies the unleaded low melting glass of a publication in either of above-mentioned claims 1-4 up to 0.05 to 100 micrometer, makes this 1 weight, adds a low expansion ceramic filler up to zero to 1.5 weight, and becomes as powder.
[Claim 6]
Unleaded low melting glass for sealing processing which mixes a binder to unleaded low melting glass according to claim 1 to 5, and becomes as a paste for sealing processing.
[Claim 7]
The vacuum package which consists of glass, ceramics, and a metal is sealed using the paste for sealing processing according to claim 6, and it is 10-6. The high vacuum more than Torr is realized and it is unleaded low melting glass for sealing processing which can close discharge gas, such as an argon, Xe-Ne, and Ne-Xe-Ar.
[Claim 8]
Unleaded sealing glass for sealing processing according to claim 6 which can sealing process the vacuum package which performs this baking near crystallization initiation temperature (it borders on crystallization initiation temperature - 20 - +50 degrees), and consists of glass, ceramics, and a metal after performing temporary baking near softening temperature (it borders on softening temperature temperature - 10 - +40 degrees).